

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-073183

(43)Date of publication of application : 21.03.2001

(51)Int.Cl.

C25D 3/38

(21)Application number : 11-244582

(71)Applicant : EBARA CORP

EBARA UDYLITE KK

(22)Date of filing : 31.08.1999

(72)Inventor : ISAYAMA YASUSHI

KAMIYAMA HIROYUKI

HONGO AKIHISA

KIMIZUKA RYOICHI

MARUYAMA EMI

(54) METHOD FOR MEASURING LEVELER CONCENTRATION IN COPPER SULFATE PLATING LIQUID

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method for measuring the leveler concentration in a copper sulfate electroplating liquid which is capable of measuring the concentration of the leveler which is an additive in the copper sulfate electroplating liquid considered heretofore infeasible even by the conventional CV method or CVS method.

SOLUTION: The method for measuring the leveler concentration in the copper sulfate electroplating liquid, which measures the concentration of the additive containing nitrogen called as the leveler among the organic additives to be included in the copper sulfate electroplating liquid, consists in analyzing the concentrations of a brightening agent (a carrier), moistening agent or polarizing agent (polymer) which is another organic additive in the plating liquid, then determining the leveler concentration by the peak value area (Ar value) measurement in a peeling region by the CV method or CVS method using a calibration curve of the leveler concentration formed by the carrier and polymer concentrations.

LEGAL STATUS

[Date of request for examination] 28.01.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]	3897936
[Date of registration]	05.01.2007
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DETAILED DESCRIPTION**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention relates to the leveler density measurement approach of the plating liquid of copper-sulfate plating equipment of using the slot for wiring formed on front faces, such as a semi-conductor substrate, and a hole for filling up with copper plating.

[0002]

[Description of the Prior Art] When copper-sulfate electrolysis plating performs restoration (embedding) of the slot for wiring, or a hole on front faces, such as a semi-conductor substrate, in order in addition to the copper sulfate (CuSO_4 and $5\text{H}_2\text{O}$) which is a basic presentation, a sulfuric acid (H_2SO_4), and chlorine (Cl) to improve plating membraneous quality and to raise the restoration nature (embedding nature) of a slot or a hole, three kinds of following organic additives are made to mix in many cases.

[0003] One is a carrier (it is also called a brei toner) which makes the plating film precise and raises glossiness. Generally it exists as an anion with a sulfur compound (for example, $\text{HS-C}_n\text{H}_2\text{n-SO}_3$ Mercapto alkylsulfonic acid), the deposit of a copper ion is blocked, and detailed-ization is promoted.

[0004] The second is a polymer (it is also called a suppressor and a carrier) which enlarges activation polarization by controlling the deposit of an adsorption copper ion, and raises throwing power to a cathode surface, and, generally they are surfactants, such as PEG and PPG.

[0005] The third is a leveler which consists of a compound of nitrogen content, such as polyamine. In plating liquid, it exists as a cation.

[0006] The location where current density is high has much adsorption of the above-mentioned leveler, activation overvoltage of the place with much adsorption of a leveler increases, and a deposit of copper is controlled.

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL FIELD

[Field of the Invention] This invention relates to the leveler density measurement approach of the plating liquid of copper-sulfate plating equipment of using the slot for wiring formed on front faces, such as a semi-conductor substrate, and a hole for filling up with copper plating.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

CLAIMS**[Claim(s)]**

[Claim 1] the leveler density-measurement approach in the copper-sulfate plating liquid which measures the concentration of the additive containing the nitrogen called a leveler among the organic additives contained in copper-sulfate electrolysis plating liquid -- setting -- a valve flow coefficient (Cyclic Voltammetric) -- law or CVS (Cyclic Voltammetric Stripping) -- the leveler density-measurement approach in the copper-sulfate plating liquid characterized by to ask for the leveler concentration of this plating liquid with the peak-value area (an Ar value) in the exfoliation field of the plating liquid measured by law.

[Claim 2] In the leveler density measurement approach in the copper-sulfate plating liquid which measures the concentration of the additive containing the nitrogen called a leveler among the organic additives contained in copper-sulfate electrolysis plating liquid After analyzing the brightener (carrier), the wetting agent, or polarizer (polymer) concentration which is other organic additives of plating liquid, With the peak value area (Ar value) in the exfoliation field of the plating liquid which created the calibration curve of leveler concentration using the criteria liquid produced by this carrier concentration and polymer concentration, and was measured by the CV method or the CVS method The leveler density measurement approach in the copper-sulfate plating liquid characterized by asking for the leveler concentration of this plating liquid.

[Claim 3] In the leveler density measurement approach in the copper-sulfate plating liquid which measures the concentration of the additive containing the nitrogen called a leveler among the organic additives contained in copper-sulfate electrolysis plating liquid The measurement liquid which made the promotion additive containing the sulfur system called a carrier one 40 times the concentration [2 thru/or] of this rather than the amount of criteria is produced. By the CV method or the CVS method The leveler density measurement approach in the copper-sulfate plating liquid characterized by computing the concentration of a leveler by measuring the difference in the amount of deposits of the copper to a rotating electrode.

[Claim 4] In the leveler density measurement approach in the copper-sulfate plating liquid which measures the concentration of the additive containing the nitrogen called a leveler among the organic additives contained in copper-sulfate electrolysis plating liquid After passing an organic anion selectivity adsorption film and removing the promotion additive containing the sulfur system called a carrier out of plating liquid, by the CV method or the CVS method The leveler density measurement approach in the copper-sulfate plating liquid characterized by computing the concentration of a leveler by measuring the difference in the amount of deposits of the copper to a rotating electrode.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

PRIOR ART

[Description of the Prior Art] When copper-sulfate electrolysis plating performs restoration (embedding) of the slot for wiring, or a hole on front faces, such as a semi-conductor substrate, in order in addition to the copper sulfate (CuSO_4 and $5\text{H}_2\text{O}$) which is a basic presentation, a sulfuric acid (H_2SO_4), and chlorine (Cl) to improve plating membrane quality and to raise the restoration nature (embedding nature) of a slot or a hole, three kinds of following organic additives are made to mix in many cases.

[0003] One is a carrier (it is also called a brei toner) which makes the plating film precise and raises glossiness. Generally it exists as an anion with a sulfur compound (for example, $\text{HS-C}_n\text{H}_{2n}\text{-SO}_3$ Mercapto alkylsulfonic acid), the deposit of a copper ion is blocked, and detailed-ization is promoted.

[0004] The second is a polymer (it is also called a suppressor and a carrier) which enlarges activation polarization by controlling the deposit of an adsorption copper ion, and raises throwing power to a cathode surface, and, generally they are surfactants, such as PEG and PPG.

[0005] The third is a leveler which consists of a compound of nitrogen content, such as polyamine. In plating liquid, it exists as a cation.

[0006] The location where current density is high has much adsorption of the above-mentioned leveler, activation overvoltage of the place with much adsorption of a leveler increases, and a deposit of copper is controlled. On the contrary, there is little adsorption of a leveler and priority is given to a deposit of copper at the bottom of a detailed slot or a hole. The deposit condition of a bottom-up is said that leveling nature is excellent.

[0007] Concentration management of the additive in the plating liquid of a copper sulfate is important, when managing plating membrane quality and stopgap nature. However, there is no approach of measuring the concentration absolute magnitude of the organic compound of the minute amount in current strong acid.

[0008] the concentration analysis method of the additive in current and the plating liquid currently performed -- valve flow coefficient (Cyclic Voltammetric) -- law or CVS (Cyclic Voltammetric Stripping) -- it is the approach called law and is converting into the concentration of an additive called a deposit inhibitor or an accelerator by measuring the copper quantity which deposits in the rotating cathode electrode.

[0009] However, it was the concentration of a carrier and a polymer which can be measured by the above-mentioned approach, and measurement of the concentration of a leveler was impossible. The concentration of a leveler is a minute amount most in the three above-mentioned additives, and the polymer and the property are similar and it has been said for measurement to be impossible also by the CV method or the CVS method until now.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

EFFECT OF THE INVENTION

[Effect of the Invention] As mentioned above, as explained, according to invention given in each claim, the outstanding effectiveness that measurement of the leveler concentration in the plating liquid which was not able to be measured by the conventional CV method or the CVS method, either is attained is acquired.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] This invention was made in view of the above-mentioned point, and aims at offering the leveler density measurement approach in the copper-sulfate plating liquid which can measure the concentration of the leveler which is an additive in the copper-sulfate plating liquid said to be impossible also by a conventional CV method or the conventional CVS method.

[Translation done.]

*** NOTICES ***

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

MEANS

[Means for Solving the Problem] In order to solve the above-mentioned technical problem, invention according to claim 1 is characterized by to ask for the leveler concentration of this plating liquid in the leveler density measurement approach in the copper sulfate plating liquid which measures the concentration of the additive containing the nitrogen called a leveler among the organic additives contained in copper sulfate electrolysis plating liquid with the peak value area (Ar value) in the exfoliation field of the plating liquid measured by the CV method or the CVS method.

[0012] Moreover, invention according to claim 2 is set to the leveler density measurement approach in the copper-sulfate plating liquid which measures the concentration of the additive containing the nitrogen called a leveler among the organic additives contained in copper-sulfate electrolysis plating liquid. After analyzing the brightener (carrier), the wetting agent, or polarizer (polymer) concentration which is other organic additives of plating liquid, The calibration curve of leveler concentration is created using the criteria liquid produced by this carrier concentration and polymer concentration, and it is characterized by asking for the leveler concentration of this plating liquid with the peak value area (Ar value) in the exfoliation field of the plating liquid measured by the CV method or the CVS method.

[0013] Moreover, invention according to claim 3 is set to the leveler density measurement approach in the copper-sulfate plating liquid which measures the concentration of the additive containing the nitrogen called a leveler among the organic additives contained in copper-sulfate electrolysis plating liquid. The measurement liquid which made the promotion additive containing the sulfur system called a carrier one 40 times the concentration [2 thru/ or] of this rather than the amount of criteria is produced, and it is characterized by computing the concentration of a leveler by the CV method or the CVS method by measuring the difference in the amount of deposits of the copper to a rotating electrode.

[0014] The efficacy of the leveler in copper-sulfate plating liquid is not decided by leveler independent concentration, and is influenced by other carriers and the concentration of a polymer. Especially the concentration of a carrier affects leveling nature. increasing the carrier concentration in the plating liquid to analyze 2 to 40 times relatively, when non-color mold nitrides, such as polyamine, are used for a leveler -- leveling -- description becomes remarkable and a calibration curve can be drawn clearly.

[0015] Moreover, invention according to claim 4 is set to the leveler density measurement approach in the copper-sulfate plating liquid which measures the concentration of the additive containing the nitrogen called a leveler among the organic additives contained in copper-sulfate electrolysis plating liquid. After passing an organic anion selectivity adsorption film and removing the promotion additive containing the sulfur system called a carrier out of plating liquid, it is characterized by computing the concentration of a leveler by the CV method or the CVS method by measuring the difference in the amount of deposits of the copper to a rotating electrode.

[0016] the direction which brought the amount of a carrier close to zero when nitrides, such as Janus green, were used for a leveler -- leveling -- description becomes remarkable and a calibration curve can be drawn clearly. Therefore, as mentioned above, the carrier in plating liquid is removed by passing an organic anion selectivity adsorption film in plating liquid, and a calibration curve can be drawn.

[0017]

[Embodiment of the Invention] Hereafter, the example of a gestalt of operation of this invention is explained based on a drawing. Drawing 1 is drawing showing the configuration of the equipment which enforces the leveler density measurement approach in the copper-sulfate plating liquid concerning this invention.

* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the configuration of the equipment which enforces the leveler density measurement approach in the copper-sulfate plating liquid concerning this invention.

[Drawing 2] It is drawing showing the calibration curve of leveler concentration and Ar value.

[Description of Notations]

- 10 Measurement Cel
- 11 Electrode Holder
- 12 Rotating Disk Electrode
- 13 Impeller
- 14 Stirrer
- 15 Potentiostat
- 21 Low Concentration Basic Cistern
- 22 High Concentration Basic Cistern
- 23 Assay Cistern
- 24 Additive Cistern
- 25 Additive Cistern
- 26 Additive Cistern
- 27 Standard-Solution Tub
- 28 Cross Valve
- 29 Buret
- 30 Cross Valve
- 31 Buret
- 32 Cross Valve
- 33 Buret
- 34 Cross Valve
- 35 Buret
- 36 Cross Valve
- 37 Buret
- 38 Cross Valve
- 39 Buret
- 40 Cross Valve
- 41 Buret
- 42 Control Unit
- 43 Driver
- 44 Sample Tub
- 45 Sample Inlet Port
- 46 Sample Return Opening
- 47 Sample Nozzle
- 48 Buret
- 49 Cross Valve

[Translation done.]

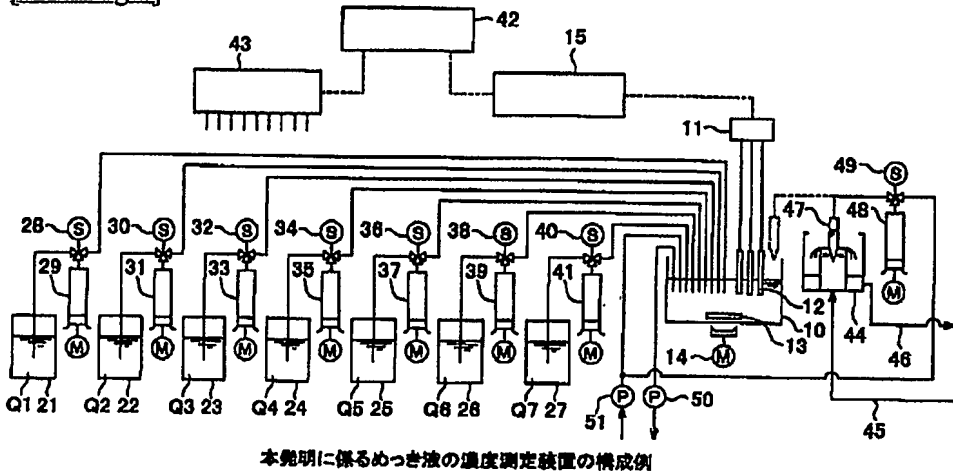
* NOTICES *

JPO and INPIT are not responsible for any damages caused by the use of this translation.

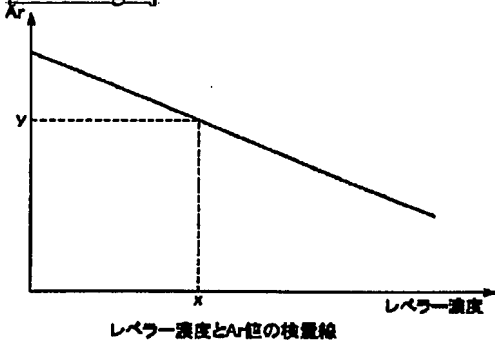
- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.**** shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]



[Drawing 2]



[Translation done.]